

07-03-00

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

UTILITY PATENT APPLICATION TRANSMITTAL 06/03/00 <small>For new nonprovisional applications under 37 C.F.R. §1.53(b))</small>		<i>Attorney Docket No.</i>	705649 US1 ML									
		<i>First Inventor or Application Identifier</i>	Klaus Binder, et al.									
		<i>Title</i>	METHOD AND APPARATUS FOR DETERMINING THE STORAGE STATE OF AN AMMONIA-STORING SCR CATALYST									
		<i>Express Mail Label No.</i>	EL536118552US									
APPLICATION ELEMENTS <small>See MPEP Chapter 600 concerning utility patent application contents.</small>		ADDRESS TO: Assistant Commissioner for Patents Box Patent Application Washington, D.C. 20231										
1. <input checked="" type="checkbox"/> *Fee Transmittal Form (e.g. PTO/SB/17) <small>(Submit an original and a duplicate for fee processing)</small> 2. <input checked="" type="checkbox"/> Specification [Total Pages 21] <small>(preferred arrangement set forth below)</small> <ul style="list-style-type: none"> -Descriptive title of the Invention -Cross References to Related Applications -Statement Regarding Fed Sponsored R&D -Reference to Microfiche Appendix -Background of the Invention -Brief Summary of the Invention -Brief Description of the Drawings (if filed) -Detailed Description -Claims(s) -Abstract of the Disclosure 3. <input checked="" type="checkbox"/> Drawing(s) (35 U.S.C. 113) [Total Sheets 7]												
4. Oath or Declaration [Total Pages 2] <ul style="list-style-type: none"> a. <input type="checkbox"/> Newly executed (original or copy) b. <input type="checkbox"/> Copy from a prior application (37 C.F.R. § 1.63 (d)) <small>(for continuation/divisional with Box 16 completed)</small> <ul style="list-style-type: none"> i. <u>DELETION OF INVENTOR(S)</u> Signed statement attached deleting inventor(s) Named in the prior application, see 37 C.F.R. § 1.63(d)(2) and 1.33 (b). 												
*NOTE FOR ITEMS 1 & 13: IN ORDER TO BE ENTITLED TO PAY SMALL ENTITY FEES, A SMALL ENTITY STATEMENT IS REQUIRED (37 C.F.R. § 1.27), EXCEPT IF ONE FILED IN A PRIOR APPLICATION IS RELIED UPON (37 C.F.R. § 1.28).												
16. If a CONTINUING APPLICATION , Check appropriate box, and supply the requisite information below and in a preliminary amendment: <input type="checkbox"/> Continuation <input type="checkbox"/> Divisional <input type="checkbox"/> Continuation-in-part (CIP) of prior application No. _____ Prior application information: Examiner _____												
FOR CONTINUATION OR DIVISIONAL APPS only: The entire disclosure of the prior application, from which an oath or declaration is supplied under Box 4b, is considered a part of the disclosure of the accompanying continuation or divisional application and is hereby incorporated by reference. The incorporation can only be relied upon when a portion has been inadvertently omitted from the submitted application parts.												
17. CORRESPONDENCE ADDRESS												
<input type="checkbox"/> Customer Number or Bar Code Label or <input checked="" type="checkbox"/> Correspondence address below <small>(Insert Customer No. or Attach bar code label here)</small>												
Name	Marc Lorelli											
	DaimlerChrysler Intellectual Capital Corporation											
Address	CIMS 483-02-19 800 Chrysler Drive											
City	Auburn Hills	State	Michigan	Zip Code								
Country	United States	Telephone	(248) 576-5294	Fax								
<table border="1"> <tr> <td>Name (Print or Type)</td> <td>Marc Lorelli</td> <td>Registration No.</td> <td>43,759</td> </tr> <tr> <td>Signature</td> <td><i>Marc Lorelli</i></td> <td>Date</td> <td>6/30/00</td> </tr> </table>					Name (Print or Type)	Marc Lorelli	Registration No.	43,759	Signature	<i>Marc Lorelli</i>	Date	6/30/00
Name (Print or Type)	Marc Lorelli	Registration No.	43,759									
Signature	<i>Marc Lorelli</i>	Date	6/30/00									

Burden Hour Statement: This form is estimated to take 0.2 hours to complete. Time will vary depending upon the needs of the individual case. Any comments on the amount of time you are required to complete this form should be sent to the Chief Information Officer, Patent and Trademark Office, Washington, D.C. 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Assistant Commissioner for Patents, Box Patent Application, Washington, D.C. 20231.

Method and apparatus for determining the storage state of an ammonia-storing SCR catalyst

5

BACKGROUND OF THE INVENTION

1. Technical Field

The invention relates to a method and an apparatus for determining the storage state of an ammonia-storing SCR catalyst.

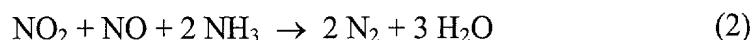
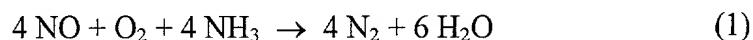
10 2. Discussion

The main sources of nitrogen oxide emissions (NOx) in the industrialized states are traffic, fossil-fired power stations and industrial installations. While the power-station and industrial emissions are being increasingly reduced, the proportion accounted for by traffic is coming 15 increasingly to the forefront.

The NOx emissions of petrol-operated spark-ignition engines can be drastically reduced by operating at $\lambda = 1$ and by post-engine emission control by means of a three-way catalyst. Owing to the principle concerned, this possibility does not exist in the case of a mixture-regulated diesel engine operated with a 20 mixture leaner than stoichiometric. On account of the high oxygen content in the exhaust gas, so far it has not been possible to produce a catalyst which can reduce the NOx emissions without the addition of reducing agents, generally hydrocarbons or ammonia-forming compounds.

To remove the nitrogen from power station emissions, SCR processes (selective catalytic reaction processes) - as described for example in DE 245888 - are used in order to convert nitrogen oxides selectively into water and nitrogen by adding the reducing agent ammonia (NH_3). Such control has proven suitable given
5 the slow changes over time in the volumetric flow of exhaust gas and NOx concentration occurring in the power station sector.

The complicated processes taking place in the SCR process can be described in a simplified form by equations (1) and (2)



Such an SCR process can also be used in a modified form for the
10 removal of nitrogen from diesel-engine exhaust gases. For use in a diesel-operated motor vehicle, in particular a commercial vehicle, numerous processes for the reduction of nitrogen oxides in exhaust gases by controlled NH_3 addition are therefore described, for example in: (1) Lepperhoff G., Schommers J.: Verhalten von SCR-Katalysatoren im dieselmotorischen Abgas [Behaviour of SCR catalysts
15 in diesel-engine exhaust gas]. MTZ 49, (1988), 17-21; (2) Hüthwohl G., Li Q., Lepperhoff G.: Untersuchung der NOx-Reduzierung im Abgas von Dieselmotoren durch SCR-Katalysatoren [Investigation of NOx reduction in the exhaust gas of diesel engines by SCR catalysts]. MTZ 54, (1992),
310-315; and (3) Maurer B., Jacob E., Weisweiler, W.: Modellgasuntersuchungen
20 mit NH_3 und Harnstoff als Reduzierungsmittel für die katalytische NOx-Reduktion [Model gas investigations with NH_3 and urea as reducing agents for catalytic NOx reduction]. MTZ 60, (1999), 398-405.

The unknown NH_3 charging state (filling level) of the SCR catalyst in non-steady-state operation proves to be problematical. It is characterized by adsorption

and desorption, which occur at different catalyst temperatures. Furthermore, the mass throughput or space velocity of the exhaust-gas flow and the content of NOx or NH₃ in the exhaust gas also affect the charging state. The ageing of the catalyst is also a factor which must not be ignored.

5 Figure 1 schematically shows a detail from a cross section of a typical SCR catalyst 10. Here, the porous catalyst material 12 is permeated by channels 14 through which the exhaust gas flows, also known as 'cells'. The cell density of such materials may be up to several hundred cells per square inch. With this structure, the porous catalyst material 12 has three tasks: primarily, the constituents 10 of the catalyst permit the desired reaction processes within the available temperature range, furthermore the extruded material provides a mechanically sturdy unit which does not require any additional support components, and finally it permits the adsorption and desorption of NH₃.

15 In the case of the supported catalyst 20 shown in Figure 2, the actual catalyst material is applied as a coating 22 to a substrate 26, for example cordierite. The substrate 26 likewise has channels 24 through which the exhaust gas flows.

A schematic overall view 30 of a catalyst is represented in Figure 3. The exhaust gas flows in the z direction.

As Figure 4 reveals, a typical catalyst material, shown here by way of 20 example, consists of the semiconductor metal oxides titanium oxide (TiO₂), vanadium oxide (V₂O₅) and tungsten oxide (WO₃). These semiconductor metal oxides can change their physical properties, in particular their electrical properties such as conductivity and permittivity, with the chemical composition or by the adsorption of NH₃ surface charges.

25 The amount of NH₃ supplied to the catalyst is partly converted directly on the surface with NOx and the remainder is adsorbed in the porous catalyst layer.

If more ammonia than can be converted by the reaction with NOx is supplied, adsorption of the excess ammonia occurs in a way corresponding to the profile sketched in Figure 5a. Figure 5a shows in case A a catalyst saturated with NH₃ at the inlet of the catalytic converter. Assumed by way of example is a maximum 5 adsorption capacity of 4 g of NH₃/kg of catalyst mass. The NH₃ mass not reacting with NOx can no longer continue to be adsorbed at the inlet of the catalytic converter and, in the example represented, only finds adsorption possible again after about 200 mm of the length of the catalyst. An 'NH₃ front' is formed, descending over the length of the catalyst from the saturated state to 0 g/kg. If the 10 excess supply of NH₃ continues, this 'NH₃ front' moves in the direction of the outlet of the catalytic converter. In case A* represented, part of the excess NH₃ is already emitted (NH₃ leakage) even though the catalyst is not yet saturated over the entire length.

The adsorption capacity of the catalyst is dependent on the catalyst 15 temperature. Case B in Figure 5a shows the amount of adsorption over the length of the catalyst for an increased temperature. With approximately equal NH₃ leakage, the integrally stored amount of NH₃ in case B is significantly reduced, see also Figure 5b.

With a controlled addition of NH₃, determination of the NH₃ filling 20 level is performed by computation and so far it has not been possible for this to be verified by measurement. To prevent NH₃ breakthrough, the adsorption capacity of the catalyst must not be used up completely on account of the relatively inaccurate computation of the filling level; as a safety measure, additional storage volume must be kept in reserve, taking up additional installation space.

25 In the event of malfunctions, so far it has not been possible for an increased filling level to be detected. Changes in the NOx emission of the engine -

for example due to changed ambient conditions (atmospheric humidity, air temperature), engine ageing, production variations, etc. -, or changes in the catalyst properties (for example ageing, reduction in the adsorption capacity) influence the mass of NH₃ to be adsorbed in the catalyst and are not covered by the filling level
5 calculation.

To ensure a correct metered amount of the reducing agent ammonia or an ammonia-forming compound, such as urea for example, the literature proposes use of one or more exhaust-gas sensors for regulating the amount of the metered agent. Thus, EP 0 554 766 A 1 presents a method which requires one or two NOx
10 sensors. DE 41 17 143 A1 proposes a method which requires one NH₃ sensor and DE 42 17 552 C1 proposes a method in which two NH₃ sensors prove to be necessary. For a further method, proposed in DE 195 36 571 A1, an NH₃ sensor is likewise indispensable.

All the methods mentioned employ control methods which are very
15 complex and scarcely cover all eventualities, since, as stated above, the charging state of the SCR catalyst is dependent on very many operating parameters, which also to a great extent involve the prehistory, i.e. earlier operating states.

If it were possible to detect the charging state of the SCR catalyst by a suitable method, it would be possible to dispense with the exhaust-gas sensors
20 mentioned above, or under certain circumstances only one NH₃ sensor would have to be fitted in the exhaust pipe as a switch, in order to diagnose a malfunction. It would be possible to dispense with complex and inaccurate control strategies. In addition, the volume of the catalytic converter (and consequently the installation space required) could be reduced by that part which has to be provided in the case
25 of exclusively open-loop controlled systems to allow additional adsorption in the

catalyst of excessively metered amounts caused by inaccurate calculation of the stored amount of NH₃ and prevent harmful NH₃ leakage.

In US 5,546,004 there is a description of a sensor for determining the storage state of an SCR catalyst. This involves measuring the electrical conductivity of a material which is identical to the SCR catalyst material with regard to its physical properties. The recording of the electrical conductivity takes place within the material at a plurality of points which are at different distances from the surface of the material around which the exhaust gas flows. The measurement of the variation in electrical conductivity in dependence on the depth of the material allows conclusions to be drawn concerning the concentration of the substance adsorbed on the sensor material.

DE 196 35 977 A1 describes a method for determining the storage state of an NOx storage catalyst. This involves sensing a physical property of the catalyst material changing chemically with the NOx storing process, a measuring pickup being applied to the NOx storage material.

Alternatively, a material which is identical with regard to its physical properties may also undergo measurement directly.

SUMMARY OF THE INVENTION

The invention is based on the object of providing a method for detecting the storage state of an SCR catalyst which can be realized cost-effectively and with which NH₃ leakage can be avoided with a great safety margin.

According to the invention, the change in at least one physical property of the SCR catalyst material, changing with the NH₃ storing process, is sensed, the measurement taking place on the SCR catalyst material itself by applying a measuring pickup to the SCR catalyst material or bringing it into direct contact

with the latter and determining the storage state, for example the filling level, on the basis of these results. Alternatively, a sensor whose function-determining element consists of the same or a similar material or a material of the same physical properties (referred to hereafter as 'substitute material') may be introduced
5 into the exhaust-gas stream, in order to infer from the physical properties of this substitute material the storage state of the SCR catalyst. In this case, the measurement takes place on the substitute material by applying the substitute material to the measuring pickup.

In both alternatives of the method, consequently the physical
10 properties of the SCR catalyst material, or of the substitute material, itself are sensed. These methods have major advantages over indirect methods, in which measuring signals outside the SCR catalyst or the substitute material (for example NH₃ breakthrough) are used to conclude their properties.

In this case, the measuring pickup is applied directly to the SCR
15 catalyst.

In an advantageous embodiment of the invention, the sensing of the physical property takes place at a plurality of points of the SCR catalyst, so that a location-dependent determination of the storage state is possible.

Additional benefits and advantages of the present invention will become
20 apparent to those skilled in the art to which this invention relates from a reading of the subsequent description of the preferred embodiment and the appended claims, taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

25 Exemplary embodiments of the invention are explained below with reference to drawings. In the drawings, Figures 1 to 5 serve for explaining the

technical principles on which the invention is based. Figures 6 to 11 show embodiments according to the invention. To be specific:

Figure 1 schematically shows a detail from a cross section of a typical SCR catalyst, a so-called 'unsupported catalyst'.

5 Figure 2 schematically shows a detail from a cross section of a further typical SCR catalyst, a so-called 'supported catalyst'.

Figure 3 shows a schematic overall view of the catalyst.

Figure 4 schematically shows the processes taking place during the selective ammonia reduction on the SCR catalyst.

10 Figures 5a and 5b show by way of example the mass of NH₃ adsorbed over the length of the catalyst for two different catalyst temperatures.

Figure 6 shows one possible arrangement of measuring pickups on the catalyst according to the invention.

15 Figure 7a shows a further possible, particularly simple, arrangement of measuring pickups on the catalyst according to the invention. Figure 7b is a perspective representation of Figure 7a which serves for a more detailed explanation.

Figure 8 shows the arrangement of two filling level sensors at the inlet and end of the catalytic converter according to the invention and the different 20 filling levels over the length of the catalyst of a partially filled catalyst.

Figure 9 shows the sectional drawing of an arrangement by way of example for measuring the complex impedance of a substitute material, which is present in the exhaust line in addition to the catalyst, according to the invention.

Figure 10 shows the sectional drawing of an arrangement by way of 25 example for measuring the thermal electromotive force of a substitute material,

which is present in the exhaust line in addition to the catalyst, according to the invention.

Figure 11 shows the sectional drawing of an arrangement by way of example for measuring the amount of adsorption of a substitute material, which is 5 present in the exhaust line in addition to the catalyst, according to the invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

In the following description, numerous specific details are set forth in order to provide a more comprehensive description of the present invention. It will be 10 apparent, however, to one skilled in the art, that the present invention may be practiced without these specific details. In other instances, specific details of well-known features have not been described so as not to obscure the present invention.

According to Figure 6, two electrodes 52, 54 are applied to a catalyst 12. In the embodiment shown, these electrodes, which are preferably but not necessarily of a porous and gas-permeable configuration, are arranged in a planar manner on two opposite walls of the catalyst. They form a lossy capacitor, which can undergo measurements with the aid of the electrical terminals 56 and 58. The complex impedance \underline{Z} between the two terminals 56 and 58 then represents a measure of the charging state of the catalyst. If accuracy so requires, recourse can 15 also be made to further measuring signals, usually present in any case, such as the exhaust-gas temperature, catalyst temperature, air ratio λ , engine speed, load moment or air mass stream, in order with the aid of these measured values to determine the charging state of the catalyst and consequently calculate and control the metering of the reducing agent.

20 The complex electrical impedance \underline{Z} is defined in the present application such that it also includes the electrical d.c. resistance. The complex

electrical impedance \underline{Z} is defined in this sense as the sum of the real part $\text{Re}(\underline{Z})$ and the imaginary part $\text{Im}(\underline{Z})$ of the complex impedance \underline{Z} . The electrical impedance \underline{Z} changes with the measuring frequency applied. Suitable as the frequency range is the range between 0 Hz (d.c. voltage) and an upper cut-off frequency, at which the
5 wavelength corresponding to the measuring frequency is significantly less than the dimensions of the measuring arrangement. Preferably, a suitable measuring frequency will be selected and the complex impedance determined from the real part and imaginary part at this frequency, or a measuring signal derived from both or one of these two variables will be recorded. The typical measured variables
10 may be: the amount of the complex impedance $|\underline{Z}|$, the d.c. resistance, the capacitance, the unbalance of an electrical bridge circuit, the loss factor or the off-resonance of a resonant circuit.

Alternatively, the electrodes may also comprise a structure, of whatever kind, that allows the electrical properties of the catalyst material to be
15 diagnosed. Figure 7a shows an inter-digital capacitor arrangement 52 applied to the catalyst, which has the advantage that an electrode arrangement has to be applied only on one side. The contacting with the supply leads 66 and 68 can then likewise take place from one side. Figure 7b illustrates this by the perspective representation. In Figure 7b, only the inter-digital capacitor arrangement itself is
20 sketched; the catalyst material has not been depicted for the sake of overall clarity. The contacting may take place, for example, from the front, since the electrical supply leads 86 and 88 have been chosen to be just long enough to reach the front edge of the catalyst.

Likewise possible is an arrangement of a measured-value pickup in the
25 form of an electrical conductor loop, which is appropriate if the catalyst material is sufficiently lossy and sufficiently electrically conductive.

Measuring pickups may also be applied at a plurality of locations of the catalyst, so that a determination of the charging state is possible not only with respect to time but also with respect to location. It is possible here for measuring pickups to be applied both along the exhaust-gas stream, i.e. in the z direction
5 according to Figure 3, or at various x or y values, in order to measure the locally changing charge distribution.

In a particularly simply structured arrangement, two or more measuring pickups may be provided at different z values along the exhaust-gas stream, the first being placed for example near the inlet of the catalytic converter
10 and the second for example in the last quarter of the catalyst, to allow, as sketched in Figure 8, determination of on the one hand the amount of adsorption in the saturated state (inlet of the catalytic converter) and in addition the safety margin against NH₃ leakage (near the outlet of the catalytic converter). The comparison of the actual NH₃ level in the saturated state (inlet of the catalytic converter) with a
15 temperature-dependent desired value allows conclusions to be drawn, for example concerning the ageing state or concerning damage to the catalyst, and makes it possible to adapt the metered amount correspondingly, right up to the emergency function. The NH₃ level in the region of the outlet of the catalytic converter provides information on the safety margin against NH₃ breakthrough. If a
20 temperature-dependent desired value is exceeded, a reduction in the metered amount is directly possible, and it is also conceivable to regulate the filling level within narrow limits around the prescribed desired value.

In a further configuration, the catalyst itself is not provided with measuring pickups (for example with electrodes), but instead a sensor whose
25 function-determining element consists of a substitute material is introduced into the catalyst. Here, too, a single sensor may be introduced or a plurality of

locationally distributed sensors may be introduced. Figure 9 shows the sectional drawing of an arrangement by way of example for measuring the complex impedance of the substitute material, which is present in addition to the catalyst in the exhaust line. The basic construction of the arrangement is similar to the arrangements in EP 0 426 989 A1 or US 5,143,696 or in Plog C., Maunz W., Kurzweil P., Obermeier E., Scheibe C.: Combustion gas sensitivity of zeolite layers on thin-film capacitors. Sensors and Actuators B 24-25 (1995) 403-406. A layer 96 is applied to a transducer 90, comprising a heater 98 on the underside of a substrate 92 - preferably made of ceramic, quartz or silicon - and a suitable electrode structure 94 (preferably in an inter-digital structure) on the upper side of the substrate. Lines provided on the transducer 90 allow the electrical impedance to be measured. The arrangement is installed in a suitable housing and is positioned in the exhaust line in the way described above. By contrast with the literature references referred to above, the layer 96 does not consist of a gas-selective material, but of the substitute material for the SCR catalyst. Therefore, the charging state can be detected with the aid of an arrangement of this type. If need be, a plurality of such arrangements may also be introduced into the catalyst at various locations. The explanatory comments made above apply in this respect.

The electrical heater 98 comprises, for example, 100 nm to 20 μm thick sheets of metal, for example platinum. The substitute material 96 has, for example, a layer thickness of between 100 nm and 1000 μm .

The electrode structure 94, for example made of a metal, has for example a layer thickness of 100 nm to 100 μm , depending on the technology.

To be able to measure the physical properties of the catalyst which characterize the charging state, other electrical measured variables may also be used, for example the Seebeck coefficient (also known as the thermal

electromotive force), or the response to temperature changes of the electrical variables referred to above.

Further non-electrical measured variables which may be used, by way of example, are the change in mass or volume.

5 The plan view of an arrangement given by way of example of how the charging state can be detected by means of measuring the thermal electromotive force is sketched in Figure 10. A layer of the substitute material 101 is applied to a transducer 100, comprising a heater (not represented) on the underside of an electrically insulating substrate 102 (preferably made of ceramic, quartz or silicon) and thermocouples 104, 106, 108, 110 on the upper side of the substrate. The electrical heater comprises, for example, 100 nm to 100 μm thick sheets of metal. The metallic conductors 104 and 106 as well as 108 and 110 are electrically connected to one another at the contact points and each form a pair of thermocouples. Typical suitable combinations of materials for the pairs of thermocouples are NiCr/Ni or T/TRh. Lines provided on the transducer 100 allow the voltages U_1 (voltage between 108 and 110) and U_2 (voltage between 104 and 106) to be measured. The arrangement is installed in a suitable housing and positioned in the exhaust line in such a way that the layer of substitute material 101 is exposed to the exhaust gas. The heater structure is designed in such a way that 10 different temperatures occur at the contact points of the two pairs of thermocouples. The difference in the voltages U_1 and U_2 is proportional to the temperature difference ΔT at the contact points - provided that the temperatures at the contact points do not differ too much. The proportionality factor results from 15 the chosen combination of materials. The voltage U_3 (voltage between 106 and 108) is a linear function of the temperature difference ΔT and the thermal electromotive force of the substitute layer 101, which is a material parameter. 20 25

Therefore, the charging state can also be detected with the aid of an arrangement of this type.

The change in mass of the storage material caused by the adsorption-desorption cycles can be measured by means of piezoelectric sensors. Quartz-crystal micro-balances may be used for example for this purpose. A possible construction is sketched in Figure 11. Here, the excitation electrodes 112 and 114 of a, for example AT-cut, vibrating quartz crystal 111 (thickness shear mode oscillator) are coated on one or both sides with the substitute material 116 and 117. The change in mass, induced by adsorption or desorption of the gases to be stored in the substitute material, brings about a change in the electrical equivalent circuit diagram parameters of the crystal two-terminal network between the electrical terminals 113 and 115, characterizing the mechanical properties of the quartz crystal. The likewise changing mechanical resonant frequency of the vibrating quartz crystal can likewise be used as a measuring signal. For this purpose, the quartz crystal is to be used as a frequency-determining element of an oscillator circuit. The resulting shift in the oscillation frequency is proportional to the change in mass of the layer of the substitute material wetting the quartz crystal and consequently characterizes the charging state of the catalyst.

When the propagation path of the surface wave of a surface wave sensor (SAW = Surface Acoustic Wave) is coated with the substitute material, the propagation rate of the surface wave changes with the storage state of the coating material. The resultant change in frequency of an SAW oscillator arrangement can likewise be used as a measuring signal for the charging state.

The foregoing description constitutes the preferred embodiments devised by the inventors for practicing the invention. It is apparent, however, that the invention is susceptible to modification, variation and change that will be obvious

to those skilled in the art. Inasmuch as the foregoing description is intended to enable one skilled in the pertinent art to practice the invention, it should not be construed to be limited thereby but should be construed to include such aforementioned obvious variations and be limited only by the proper scope or fair

5 meaning of the accompanying claims.

DaimlerChrysler AG
Stuttgart

What is Claimed is:

1. Method for determining the storage state of an ammonia-adsorbing SCR catalyst, wherein the change in at least one physical property of the SCR catalyst changes on account of the the NH₃ storing process, said method comprising:

5 applying a measuring pickup to the SCR catalyst;
sensing a physical property of the SCR catalyst from said measuring pickup; and

determining the storage state on the basis of said physical property.

10

2. Method according to Claim 1, wherein the sensing of a physical property is carried out at a plurality of points of the SCR catalyst.

- 15 3. Method according to Claim 2, wherein the physical property is an electrical property of the SCR catalyst or the SCR catalysts' response to temperature changes.

4. Method according to Claim 3, wherein the electrical impedance of the SCR catalyst is sensed.

20

5. Method according to Claim 4, wherein the sensing of the impedance takes place at one or more frequencies from the frequency range between 0 Hz and an upper cut-off frequency, at which the wavelength corresponding to the

measuring frequency is significantly less than the dimensions of the measuring arrangement.

6. Method according to Claim 4, wherein the sensing of the electrical

5 impedance occurs with either two electrodes, a conductor loop, or an inter-digital structure.

7. Method according to Claim 6, wherein one of said plurality of points is near the inlet of the SCR catalyst, and another of said plurality of points is disposed in the rearward quarter of the SCR catalyst.

10

8. Method according to Claim 1, wherein the thermal electromotive force of the SCR catalyst material is sensed.

9. Method according to Claim 1, wherein the change in mass or volume
15 of the SCR catalyst is sensed.

20

25

10. Method for determining the storage state of an ammonia-adsorbing SCR catalyst, said SCR catalyst adapted for use in an exhaust gas stream, said method comprising:

5 placing a material identical or similar to the SCR catalyst material with regard to its physical properties, said material being arranged in the exhaust-gas stream in addition to the SCR catalyst, said material includes at least one physical property that changes with the NH₃ storing process;

10 applying said material to a measuring pickup;

15 sensing a physical property of said material from said measuring pickup;

and

determining the storage state on the basis of said physical property.

11. Method according to Claim 10, wherein the sensing of a physical property is carried out at a plurality of points of the SCR catalyst.

15

12. Method according to Claim 11, wherein said physical property is an electrical property of the material or said material's response to temperature.

13. Method according to Claim 12, wherein the electrical impedance of the
20 substitute material is sensed.

14. Method according to Claim 13, wherein the sensing of the impedance takes place at one or more frequencies from the frequency range between 0 Hz, i.e. d.c. voltage, and an upper cut-off frequency, at which the wavelength corresponding to the measuring frequency is significantly less than the dimensions
25 of the measuring arrangement.

15. Apparatus for carrying out the method according to Claim 14, wherein
the measuring pickup for sensing the complex electrical impedance includes a
substrate having two generally flat sides, on one flat side either a conductor or
5 electrode structure is applied, and on the other flat side an electrical heater is
applied, the material being applied on the flat side that is provided with the
conductor or electrode structure.
16. Apparatus according to Claim 15, wherein either the conductor or
10 electrode structure is an inter-digital structure.
17. Apparatus according to Claim 16, wherein the substrate is selected
from silicon, quartz or a ceramic, and the electrical heater has 100 nm to 50 μm
thick sheets of metal, and the conductor or electrode structure is constructed of
15 metal and has a layer thickness of between 100 nm and 100 μm and the material
has a layer thickness of between 100 nm and 1000 μm .
18. Method according to Claim 10, wherein the change in the thermal
electromotive force of the substitute material is sensed.
20
19. Apparatus for carrying out the method according to Claim 18, wherein
the measuring pickup for sensing the thermal electromotive force includes a
substrate having two generally flat sides, on one flat side an electrical heater is
applied on the other flat side the material and at least two pairs of thermocouples
25 are applied.

20. Apparatus according to Claim 19, wherein the substrate consists of silicon, quartz or a ceramic, and the electrical heater has 100 nm to 100 µm thick sheets of metal.
- 5 21. Method according to Claim 10, wherein the change in mass or volume is sensed.
22. Apparatus for carrying out the method according to Claim 21, wherein the measuring pickup for sensing the change in mass of the material includes a vibrating quartz crystal on which electrical excitation electrodes are applied on 10 both sides, the material being applied at least on one excitation electrode.
23. Apparatus for carrying out the method according to Claim 21, wherein the measuring pickup for recording the change in mass of the substitute material is constructed as follows: the laminar substitute material forms within a surface wave 15 sensor the propagation path of a surface wave.

DaimlerChrysler AG
Stuttgart

Abstract

A method for determining the storage state of an ammonia-storing SCR catalyst, the change in at least one physical property of the SCR catalyst material, changing with the NH₃ storing process, being sensed, the measurement taking place on the SCR catalyst material itself by applying a measuring pickup to the SCR catalyst or bringing it into direct contact with the latter and determining the storage state on the basis of these results. In an alternative embodiment, a material identical or similar to the SCR catalyst material with regard to its physical properties is arranged in the exhaust-gas stream in addition to the SCR catalyst material, and the change in at least one physical property of this substitute material changing with the NH₃ storing process, is sensed, the measurement taking place on the substitute material itself by applying the substitute material to the measuring pickup or bringing it into direct contact with the latter and determining the storage state of the SCR catalyst on the basis of these results.

Fig. 1

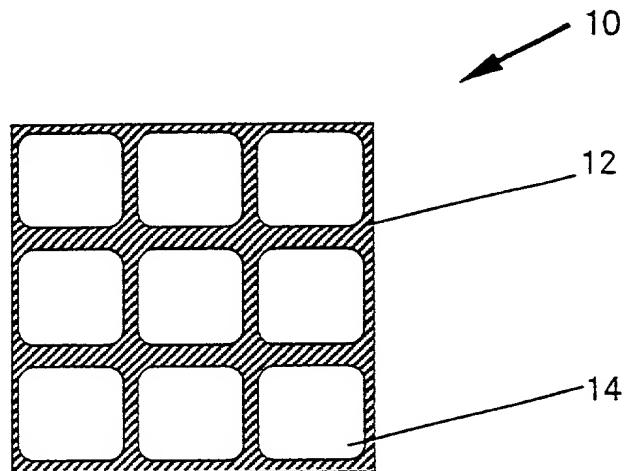


Fig. 2

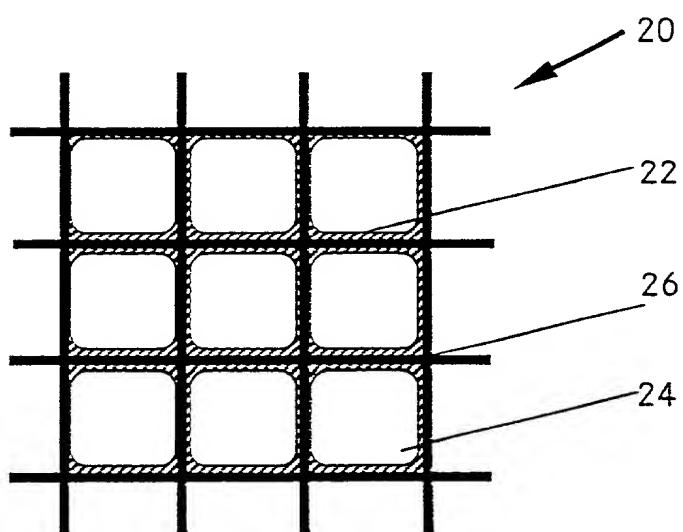


Fig. 3

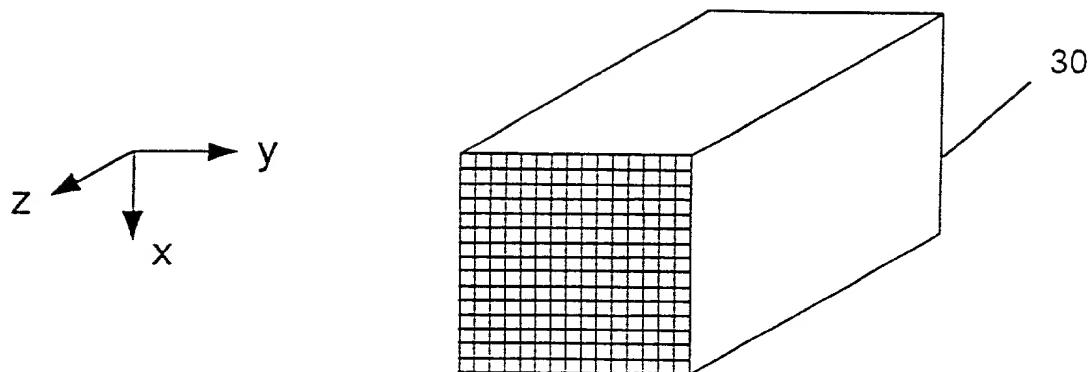
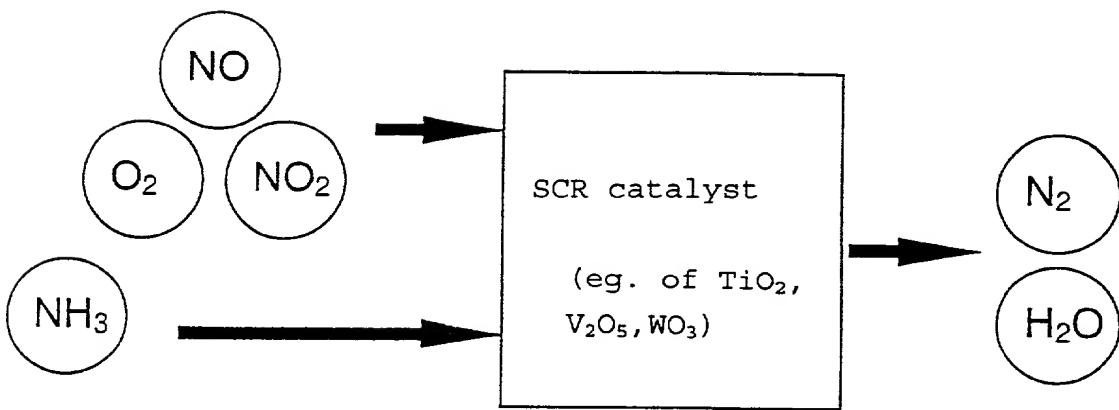


Fig. 4



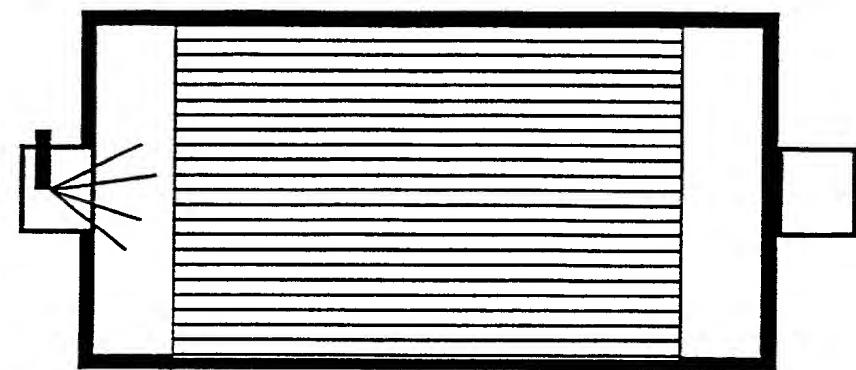


Fig. 5a

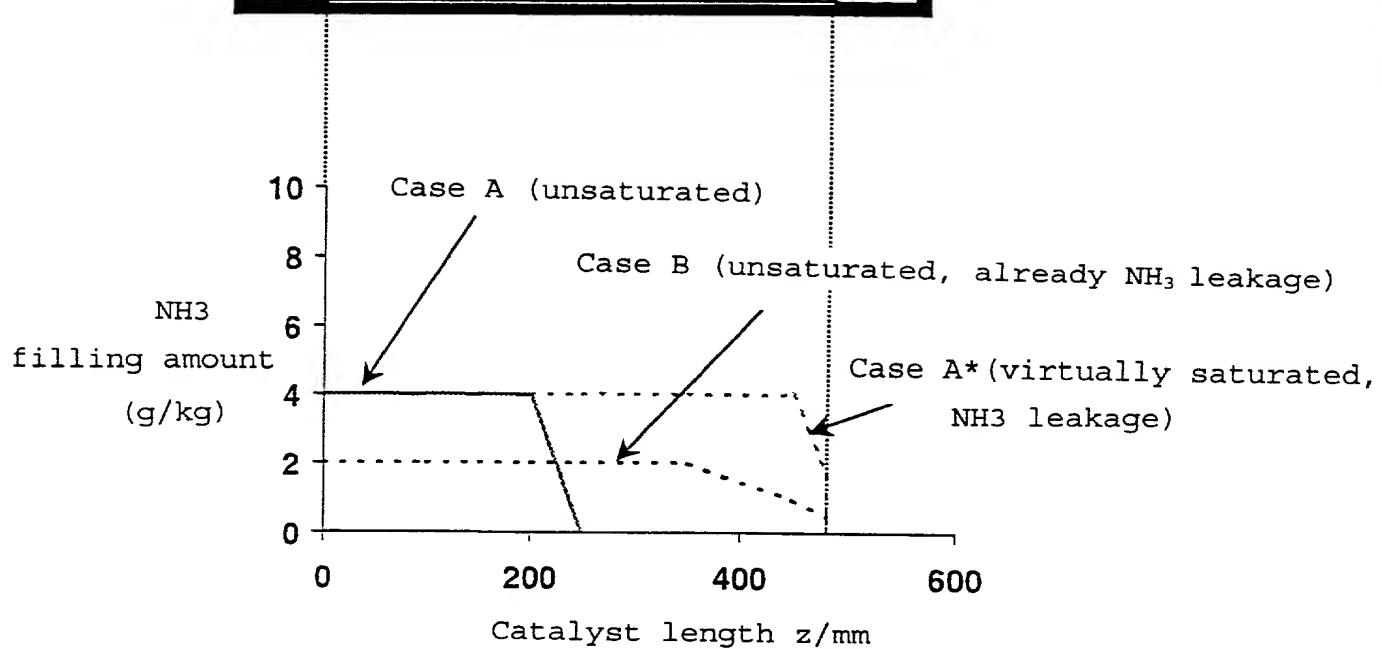


Fig. 5b

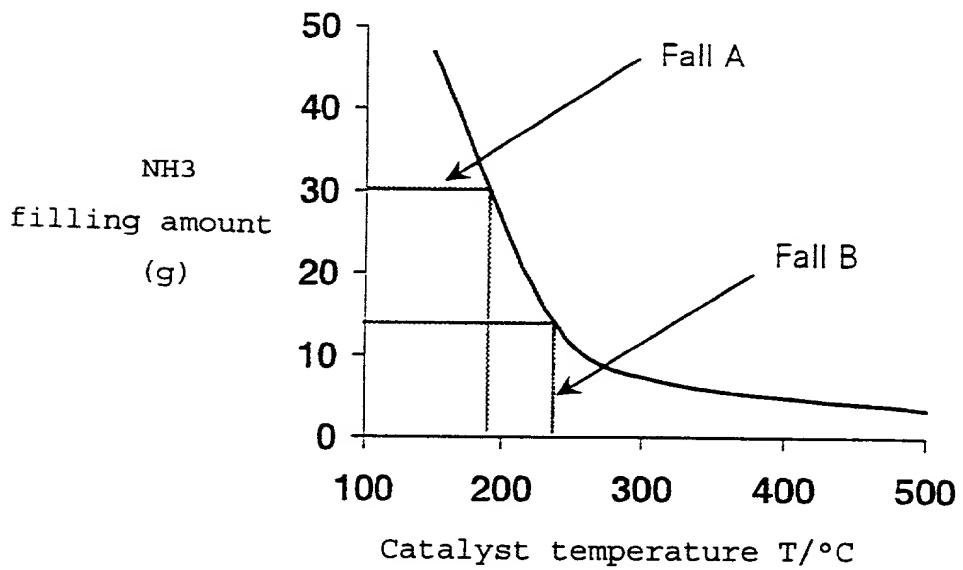


Fig. 6

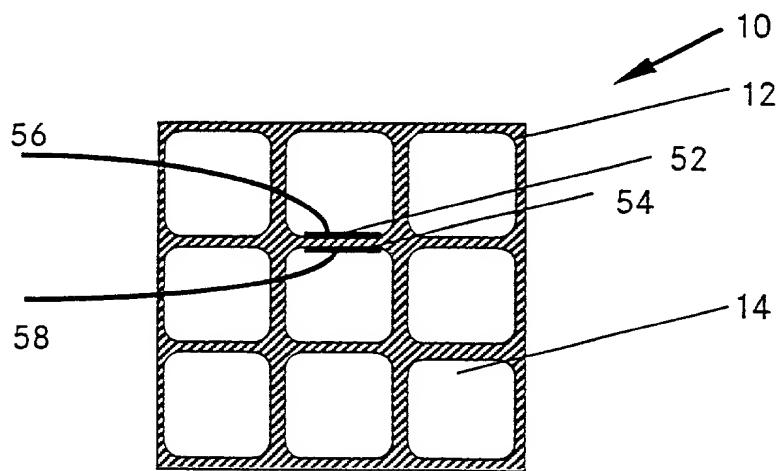


Fig. 7a

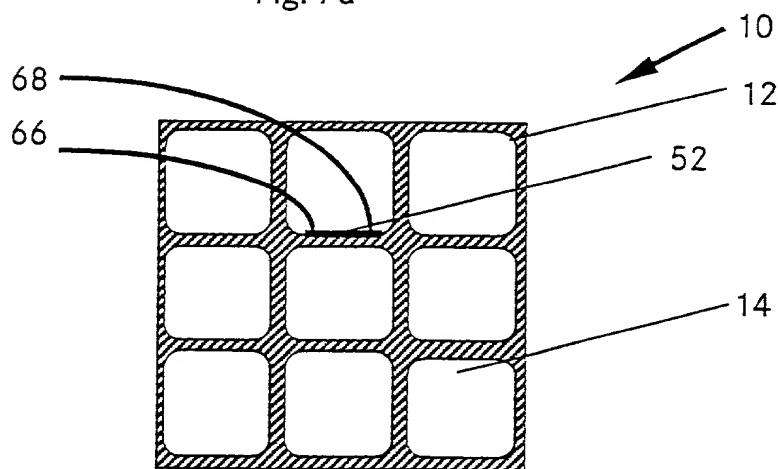


Fig. 7b

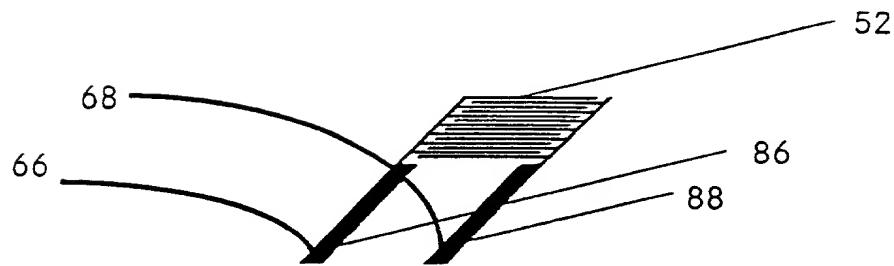


Fig. 8

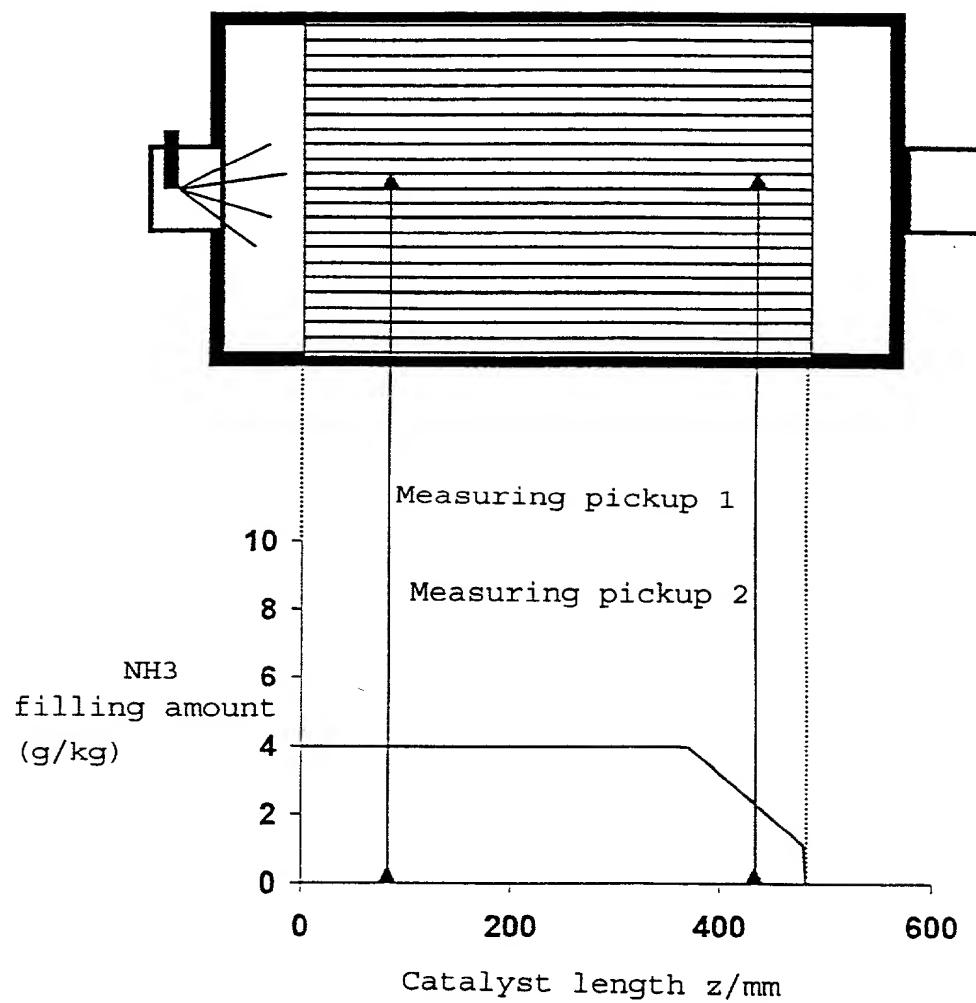


Fig. 9

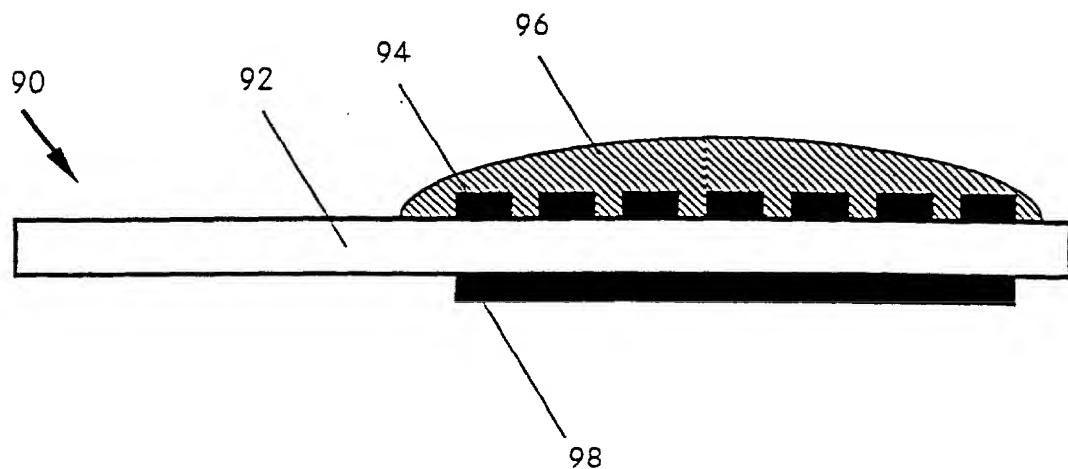


Fig. 10

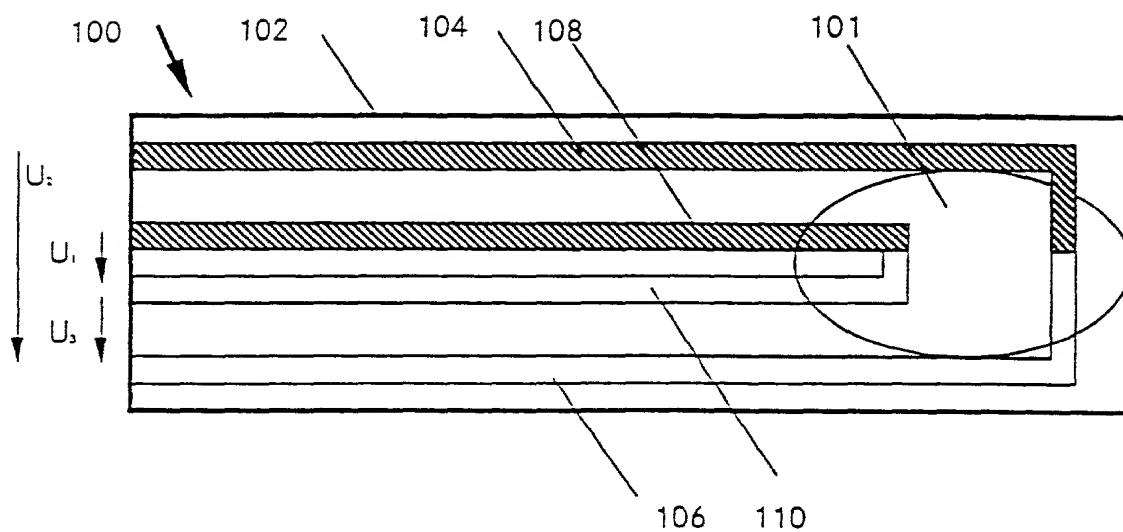
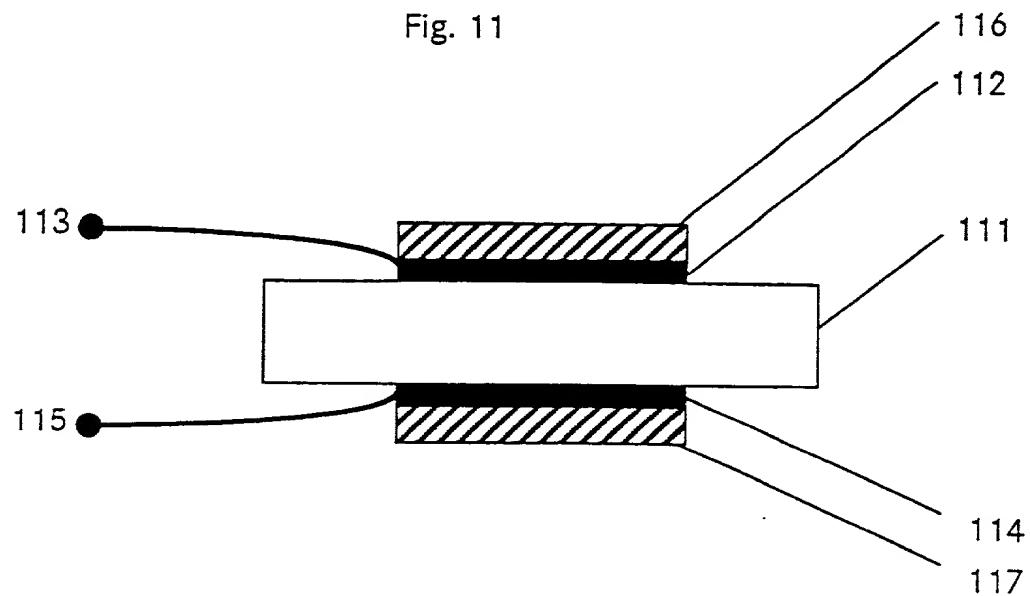


Fig. 11



Declaration and Power of Attorney for Patent Application

Erklärung für Patentanmeldungen mit Vollmacht

German Language Declaration

Als nachstehend benannter Erfinder erkläre ich hiermit an Eides Statt:

As a below named inventor, I hereby declare that:

- | | |
|--------------------------------|----------------------------------|
| 1) Klaus Binder | 5) Klaus-Jürgen Marquardt |
| 2) Tillmann Braun | 6) Ralf Moos |
| 3) Michael-Rainer Busch | 7) Carsten Plog |
| 4) Aleksandar Knezevic | |

daß mein Wohnsitz, meine Postanschrift und meine Staatsangehörigkeit den im nachstehenden nach meinem Namen aufgeführten Angaben entsprechen, daß ich nach bestem Wissen der ursprüngliche, erste und alleinige Erfinder (falls nachstehend nur ein Name angegeben ist) oder ein ursprünglicher, erster und Miterfinder (falls nachstehend mehrere Namen aufgeführt sind) des Gegenstandes bin, für den dieser Antrag gestellt wird und für den ein Patent für die Erfindung mit folgendem Titel beantragt wird:

My residence, post office address and citizenship are as stated next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

"Method and Apparatus for Determining The Storage State of an Ammonia-Storing SCR Catalyst"

deren Beschreibung hier beigefügt ist, es sei denn (in diesem Falle Zutreffendes bitte ankreuzen), diese Erfindung

the specification of which is attached hereto unless the following box is checked:

- wurde angemeldet am _____ unter der US-Anmeldenummer oder unter der Internationalen Anmeldenummer im Rahmen des Vertrags über die Zusammenarbeit auf dem Gebiet des Patentwesens (PCT)
_____ und am _____ abgeändert (falls zutreffend).

was filed on June 30, 2000 as United States Application Number or PCT International Application Number _____ and was amended on _____ (if applicable).

Ich bestätige hiermit, daß ich den Inhalt der oben angegebenen Patentanmeldung, einschließlich der Ansprüche, die eventuell durch einen oben erwähnten Zusatzantrag abgeändert wurde, durchgesehen und verstanden habe.

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

Ich erkenne meine Pflicht zur Offenbarung jeglicher Informationen an, die zur Prüfung der Patentfähigkeit in Einklang mit Titel 37, Code of Federal Regulations, § 1.56 von Belang sind.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56.

German Language Declaration

Ich beanspruche hiermit ausländische Prioritätsvorteile gemäß Title 35, US-Code, § 119(a)-(d), bzw. § 365(b) aller unten aufgeführten Auslandsanmeldungen für Patente oder Erfinderurkunden, oder § 365(a) aller PCT internationalen Anmeldungen, welche wenigstens ein Land ausser den Vereinigten Staaten von Amerika benennen, und habe nachstehend durch ankreuzen sämtliche Auslandsanmeldungen für Patente bzw. Erfinderurkunden oder PCT internationale Anmeldungen angegeben, deren Anmeldetag dem der Anmeldung, für welche Priorität beansprucht wird, vorangeht.

Prior Foreign Applications (Frühere ausländische Anmeldungen)

199 31 007.6-52	GERMANY
(Number) (Nummer)	(Country) (Land)
(Number) (Nummer)	(Country) (Land)

Ich beanspruche hiermit Prioritätsvorteile unter Title 35, US-Code, § 119(e) aller US-Hilfsanmeldungen wie unten aufgezählt.

(Application No.)
(Aktenzeichen)

(Application No.)
(Aktenzeichen)

Ich beanspruche hiermit die mir unter Title 35, US-Code, § 120 zustehenden Vorteile aller unten aufgeführten US-Patentanmeldungen bzw. § 365(c) aller PCT internationalen Anmeldungen, welche die Vereinigten Staaten von Amerika benennen, und erkenne, insofern der Gegenstand eines jeden früheren Anspruchs dieser Patentanmeldung nicht in einer US-Patentanmeldung, bzw. PCT internationalen Anmeldung in einer gemäß dem ersten Absatz von Title 35, US-Code, § 112 vorgeschriebenen Art und Weise offenbart wurde, meine Pflicht zur Offenbarung jeglicher Informationen an, die zur Prüfung der Patentfähigkeit in Einklang mit Title 37, Code of Federal Regulations, § 1.56 von Belang sind und die im Zeitraum zwischen dem Anmeldetag der früheren Patentanmeldung und dem nationalen oder im Rahmen des Vertrags über die Zusammenarbeit auf dem Gebiet des Patentwesens (PCT) gültigen internationalen Anmeldetags bekannt geworden sind.

(Application No.)
(Aktenzeichen)

(Filing Date)
(Anmeldetag)

Ich erkläre hiermit, daß alle in der vorliegenden Erklärung von mir gemachten Angaben nach bestem Wissen und Gewissen der Wahrheit entsprechen, und ferner daß ich diese eidesstattliche Erklärung in Kenntnis dessen ablege, daß wissentlich und vorsätzlich falsche Angaben oder dergleichen gemäß § 1001, Title 18 des US-Code strafbar sind und mit Geldstrafe und/oder Gefängnis bestraft werden können und daß derartige wissentlich und vorsätzlich falsche Angaben die Rechtswirksamkeit der vorliegenden Patentanmeldung oder eines aufgrund deren erteilten Patentes gefährden können.

I hereby claim foreign priority under Title 35, United States Code, § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

Priority Not Claimed
Priorität nicht beansprucht

July 6, 1999
(Day/Month/Year Filed)
(Tag/Monat/Jahr der Anmeldung)

(Day/Month/Year Filed)
(Tag/Monat/Jahr der Anmeldung)

I hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below.

(Filing Date)
(Anmeldetag)

(Filing Date)
(Anmeldetag)

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

(Status) (patented, pending, abandoned)
(Status) (patentiert, schwebend, aufgegeben)

(Status) (patented, pending, abandoned)
(Status) (patentiert, schwebend, aufgegeben)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

German Language Declaration

VERTRETUNGSVOLMACHT: Als benannter Erfinder beauftrage ich hiermit den (die) nachstehend aufgeführten Patentanwalt (Patentanwälte) und/oder Vertreter mit der Verfolgung der vorliegenden Patentanmeldung sowie mit der Abwicklung aller damit verbundenen Angelegenheiten vor dem US-Patent- und Markenamt:
(Name(n) und Registrationsnummer(n) auflisten)

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith:

William J. Coughlin,	Registration No. 29,143
Donna L. Berry,	Registration No. 36,451
Mark P. Calcattera,	Registration No. 30,363
Marc Lorelli,	Registration No. 43,759
Kenneth H. Maclean,	Registration No. 25,236
Roland A. Fuller III,	Registration No. 31,160
Lawrence J. Shurupoff,	Registration No. 30,219
Jennifer M. Stec,	Registration No. 35,379
James R. Yee,	Registration No. 34,460

Send Correspondence to:

Postanschrift:

Marc Lorelli
DaimlerChrysler Corporation
800 Chrysler Drive East, CIMS 483-02-19
Auburn Hills, Michigan 48326

Direct Telephone Calls to: (name and telephone number)

Telefonische Auskünfte: (name and telefonenumber)

Marc Lorelli
(248) 576-5294

Full name of sole or first inventor:

Vor- und Zuname des einzigen oder ersten Erfinders: Klaus Binder

Inventor's signature: _____ Date: _____

Unterschrift des Erfinders: _____ Datum: _____

Place of Residence:

Wohnsitz : Deizisau, Germany Staatsangehörigkeit: German

Post Office Address:

Postanschrift: Schurwaldblick 7, 73779 Deizisau, Germany

Full name of second joint inventor, if any:

Vor- und Zuname des zweiten Miterfinders (falls zutreffend): Tillmann Braun

Inventor's signature: _____ Date: _____

Unterschrift des Erfinders: _____ Datum: _____

Place of Residence:

Wohnsitz : Berglen, Germany Staatsangehörigkeit: German

Post Office Address:

Postanschrift: Frühlingsweg 1, 73663 Berglen, Germany

Full name of third joint inventor, if any:

Vor- und Zuname des dritten Miterfinders (falls zutreffend): Michael-Rainer Busch

Inventor's signature: _____ Date: _____

Unterschrift des Erfinders: _____ Datum: _____

Place of Residence:

Wohnsitz : Ebersbach, Germany Staatsangehörigkeit: German

Post Office Address:

Postanschrift: Panoramastrasse 7/6, 73061 Ebersbach, Germany

German Language Declaration

Full name of fourth joint inventor, if any:

Vor- und Zuname des vierten Miterfinders (falls zutreffend): Aleksandar Knezevic

Inventor's signature:

Date:

Unterschrift des Erfinders:

Datum:

Place of Residence:

Citizenship:

Wohnsitz : Kirchheim / Teck, Germany

Staatsangehörigkeit: German

Post Office Address:

Postanschrift: Charlottenstrasse 31, 73230 Kirchheim / Teck, Germany

Full name of fifth joint inventor, if any:

Vor- und Zuname des fünften Miterfinders (falls zutreffend): Klaus-Jürgen Marquardt

Inventor's signature:

Date:

Unterschrift des Erfinders:

Datum:

Place of Residence:

Citizenship:

Wohnsitz : Remshalden, Germany

Staatsangehörigkeit: German

Post Office Address:

Postanschrift: Schönbühlstrasse 23, 73630 Remshalden, Germany

Full name of sixth joint inventor, if any:

Vor- und Zuname des sechsten Miterfinders (falls zutreffend): Ralf Moos

Inventor's signature:

Date:

Unterschrift des Erfinders:

Datum:

Place of Residence:

Citizenship:

Wohnsitz : Friedrichshafen, Germany

Staatsangehörigkeit: German

Post Office Address:

Postanschrift: Muntenriedstrasse 8, 88048 Friedrichshafen, Germany

Full name of sixth joint inventor, if any:

Vor- und Zuname des sechsten Miterfinders (falls zutreffend): Carsten Plog

Inventor's signature:

Date:

Unterschrift des Erfinders:

Datum:

Place of Residence:

Citizenship:

Wohnsitz : Markdorf, Germany

Staatsangehörigkeit: German

Post Office Address:

Postanschrift: Döllerstrasse 13, 88677 Markdorf, Germany